04 p-Block (Group-13 & 14)

Inert pair effect

	Group-13	Group-14	Group-15
(group oxidation state)	$\underset{+3}{ns^2np^1}$	$\underset{+4}{ns^2np^2}$	$\underset{+5}{ns^2np^3}$

⇒ While moving down the group the stability of lower oxidation state (2 less than group oxidation state) progressively increases and for the last element of the group the stability of lower oxidation state increases than the group oxidation state. **This is called inert pair effect.**

Group-13		Group-14		Group-15	
B	**+3**	**C**	**+4**	**N**	**+5**
Al	**+3**	**Si**	**+4**	**P**	**+5**
Ga	**+3 > +1**	**Ge**	**+4 > +2**	**As**	**+5 > +3**
In	**+3 > +1**	**Sn**	**+4 > +2**	**Sb**	**+5 > +3**
Tl	**+3 < +1**	**Pb**	**+4 < +2**	**Bi**	**+ 5 < +3**

Reason : As we move down the group there is presence of d & f-orbitals in inner shells which have poor shielding effect hence Z_{eff} increases. As a result the ns^2 electron pair becomes more and more tightly held to the nucleus and becomes inert /passive towards bonding.

⇒ For the last element group oxidation state is highly oxidising in nature.

Examples :

1. $PbCl_2$ is more stable than $PbCl_4$.

2. TlCl is more stable than $TlCl_3$.

3. $GaCl_3$ is more stable than $TlCl_3$.

4. $SnCl_4$ is more stable than $PbCl_4$.

5. Thallium (III) iodide does not exist.

6. PbF_4, $PbCl_4$ exist but $PbBr_4$ and PbI_4 does not exist.

7. Among pentahalides of Bi only BiF_5 exists.

∵ $F^- < Cl^- < Br^- < I^-$

$\longrightarrow$

reducing nature

due to strong oxidising nature of Pb^{+4} and strong reducing nature of Br^- and I^-, $PbBr_4$ and PbI_4 does not exist while Cl^- and F^- cannot reduce Pb^{+4}

Illustrations

Illustration 1: **Stability of trivalent cations of group III A will be in order.**

(1) $Ga^{3+} < In^{3+} < T\ell^{3+}$

(2) $Ga^{3+} > In^{3+} > T\ell^{3+}$

(3) $Ga^{3+} > In^{3+} < T\ell^{3+}$

(4) $T\ell^{3+} > In^{3+} < Ga^{3+}$

Solution: **Ans. (2)**

Illustration 2: **Aluminium and Ga have the same covalent radius because of –**

(1) Greater shielding power of s–electrons of Ga atoms.
(2) Poor shielding power of s–electrons of Ga atoms.
(3) Poor shielding power of d–electrons of Ga atoms.
(4) Greater shielding power of d–electrons of Ga atoms.

Solution: **Ans. (3)**

BEGINNER'S BOX-1

1. Which halide is unknown ?
(1) Tl(III) iodide (2) In(III) bromide
(3) Ga(III) fluoride (4) B(III) chloride

2. There is a tendency for the elements of groups 13 to 15 of higher periods, particularly period 6, to form compounds with ions having a positive charge of _____ less than the group oxidation number.
(1) One (2) Three (3) Four (4) Two

3. Which oxidation states are more characteristic for lead and tin ?
(1) For lead + 4, for tin + 2 (2) For lead + 2, for tin + 2
(3) For lead + 4, for tin + 4 (4) For lead + 2, for tin + 4

4. Which of the following pentahalide can not be formed :-
(1) PCl_5 (2) $AsCl_5$ (3) $SbCl_5$ (4) $BiCl_5$

Back bonding

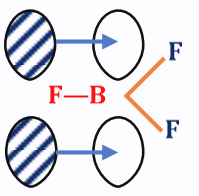
Definition : It is an additional bond which is formed between 2 adjacent bonded atoms in a covalent molecule/ion by collateral overlapping.

Conditions for back bonding :

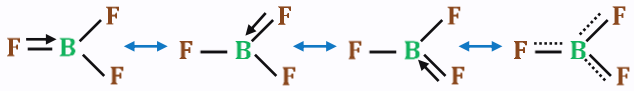
(i) One bonded atom must possess vacant orbital and the other bonded atom must possess lone pair.

(ii) Both bonded atoms must belong to 2nd period or one bonded atom must belong to 2nd period and other belong to 3rd period.

As a result of back bonding between the bonded atoms, bond length decreases and bond energy increases.



F-donor
B-acceptor



(B–F) B.O = 4/3 = 1.33

Types of back bonding :

Based on type of orbitals involved in overlapping
2 types of back bonding is possible

(1) pπ-pπ back bonding

(2) pπ-dπ back bonding

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(1) pπ-pπ back bonding : It is formed by the sidewise overlapping of two p orbitals.

Order of strength : **2p – 2p > 2p – 3p > 2p – 4p .....**

Size of orbital ↑ extent of B.B. ↓

It is used to explain following observations :-

(a) Abnormal bond length and bond energy of B-F bond in BF_3.

(b) Lewis acidic order of **Boron** and **Beryllium** halides.

BF_3 < BCl_3 < BBr_3 < BI_3

BeF_2 < $BeCl_2$ < $BeBr_2$ < BeI_2

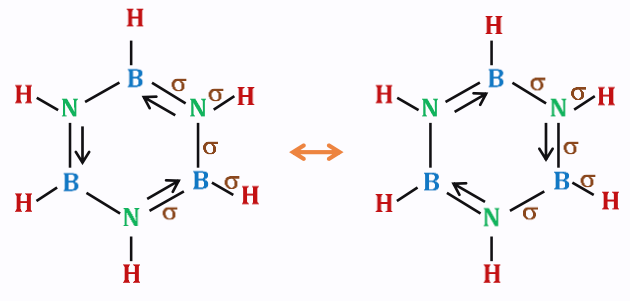
$\because$ extent of back bonding ↓

$\therefore$ Lewis acidic strength ↑

(c) Hybridisation : If a lone pair participates in back bonding then it is not considered in hybridisation.

Ex. $B_3N_3H_6$ (inorganic benzene or borazine or borazole)

Hybridisation of B as well as N is sp^2



Inorganic benzene is more reactive than organic benzene as in it the **bonds are polar,** although overall molecule is non-polar.

(d) If back bonding is present in the molecule then tendency to form dimer or polymer decreases.

Ex. BF_3, BeF_2

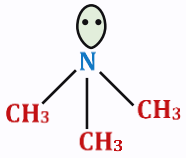
(2) pπ-dπ back bonding :

It is formed by the side wise overlapping between 2p and 3d orbitals.

It is used to explain the following observations :

(a) Hybridisation

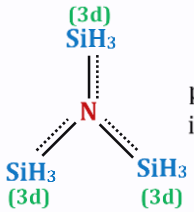
Ex. Trimethyl amine **$(CH_3)_3N$**



Back bonding is not possible due to absence of vacant orbital

- Hybridisation of N is sp^3
- Structure is trigonal pyramidal
- It is a stronger Lewis base (due to presence of l.p.)

Trisilyl amine **$(SiH_3)_3N$**



pπ—dπ back bonding is possible

- Hybridisation of N is sp^2
- Structure is trigonal planar
- It is a weaker Lewis base

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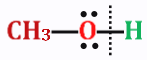
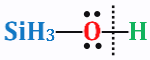
(b) Acidic strength



Methyl alcohol



Silyl alcohol

- No back bonding in conjugate base
- Less acidic

- Back bonding present in conjugate base
- More acidic

Illustrations

Illustration 3: **Identify the compounds showing back bonding in the following :**

(a) BF_3 (b) BF_4^- (c) $O(SiH_3)_2$ (d) $O(CH_3)_2$

Solution: **(a, c)**

Illustration 4: **Compare the given properties of followings compounds**

(a) BF_3, BF_4^- (bond length)

(b) BF_3, BF_4^- (bond angle)

(c) BF_3, BCl_3, BBr_3, BI_3 (Lewis acid strength)

Solution: (a) < (b) > (c) increasing order

(d) > (e) > (f) Pyramidal, Trigonal planar

BEGINNER'S BOX-2

1. In BF_3 :

(1) B-F bond has some double bond character and this bond is delocalised

(2) All the B–F bonds are single covalent in nature

(3) Bond energy and bond-length of B–F bond indicate its single bond character

(4) All of the bonds are ionic

2. Which of the following statements is incorrect in the context of the B–F bond in BF_3 :-

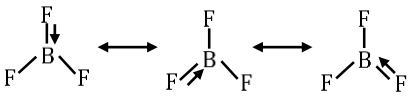
(1) All the three B–F bond lengths are equal and each of them is shorter than the sum of the covalent radii of boron and fluorine.

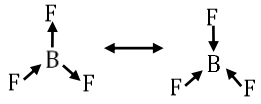
(2) The bond energy of the B–F bond is very high, higher than for any other single bond

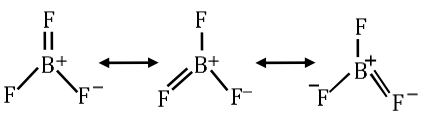
(3) The unusual shortness and strength of the B–F bond may be explained by a $p\pi$-$p\pi$ interaction between boron and fluorine atoms.

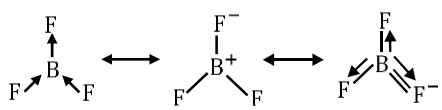
(4) The unusual shortness and strength of the bonds may be explained by a $p\pi$-$d\pi$ interaction between the atoms of boron and fluorine.

3. Which of the following structures correctly represents the boron trifluoride molecule :

(1) 

(2) 

(3) 

(4) 

4. Trisilylamine $[\ddot{N}(SiH_3)_3]$ has a

(1) Planar geometry (2) Tetrahedral geometry

(3) Pyramidal geometry (4) None of these

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Hydrolysis

Reaction of water molecules with covalent compound in such a way that H_2O molecule break into H^+ and OH^- ion.

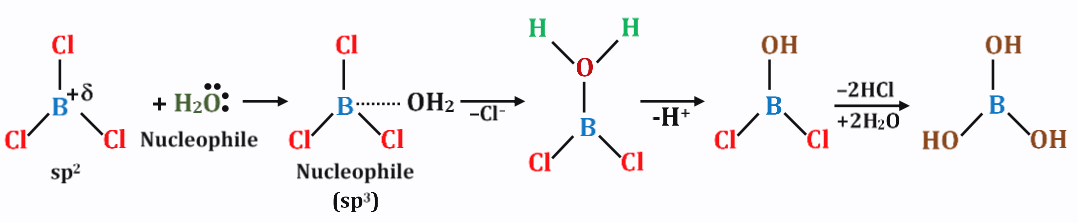
(A) Hydrolysis of halides :

Ionic Halides - Hydration

Covalent Halides - Hydrolysis

- **Condition for hydrolysis**
  - Only those halide will undergo hydrolysis in which water molecule provide LP and other molecule must have vacant orbital.

Mechanism :



Note : During hydrolysis formed intermediate involved one extra orbital than parent molecule.

- degree of hydrolysis $\propto$ covalent character $\propto \frac{1}{\text{Ionic character}}$

order of hydrolysis – $NaCl < MgCl_2 < AlCl_3 < SiCl_4$

$PCl_5 > AsCl_5 > SbCl_5 > BiCl_5$

$BF_3 < BCl_3 < BBr_3 < BI_3$

$$\underset{\text{LA LB}}{P\ Cl_3} + 3H^+\ \underset{\text{LA}}{OH^-}\ \underset{\text{LB}}{} \rightarrow 3HCl + H_3PO_3$$

$$\underset{\text{LA LB}}{B\ Cl_3} + 3H^+\ \underset{\text{LA}}{OH^-}\ \underset{\text{LB}}{} \rightarrow B(OH)_3 + 3HCl$$

- It is a neutralisation process of Lewis acid and Lewis base

(i) $AlCl_3 + 3H^+OH^- \rightarrow Al(OH)_3 + 3HCl$

(ii) $BeCl_2 + 2H^+OH^- \rightarrow Be(OH)_2 + 2HCl$

(iii) $MgCl_2 + 2H^+OH^- \rightarrow Mg(OH)_2 + 2HCl$

(B) Hydrolysis of metal carbide, metal nitride, metal hydride

(i) $AlN + 3H^+OH^- \rightarrow Al(OH)_3 + NH_3$

(ii) $CaC_2 + 2H^+OH^- \rightarrow Ca(OH)_2 + C_2H_2$

(iii) $Mg_2C_3 + 4H^+OH^- \rightarrow 2Mg(OH)_2 + C_3H_4$

(iv) $Al_4C_3 + 12H^+OH^- \rightarrow 4Al(OH)_3 + 3CH_4$

(v) $Mg_3N_2 + 6H^+OH^- \rightarrow 3Mg(OH)_2 + 2NH_3$

(vi) $Be_2C + 4HOH \rightarrow 2Be(OH)_2 + CH_4$

(vii) $NaH + H^+OH^- \rightarrow NaOH + H_2$

(viii) $CaH_2 + 2HOH \rightarrow Ca(OH)_2 + 2H_2$

(C) Metal oxide + $H_2O \rightarrow$ Base

$Na_2O + H_2O \rightarrow NaOH$

$CaO + H_2O \rightarrow Ca(OH)_2$

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(D) Non Metal oxide + $H_2O \rightarrow$ Oxy acid

$CO_2 + H_2O \rightarrow H_2CO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

Illustrations

Illustration 5: **Give the hydrolysis product of given compounds**

(a) BCl_3 (b) $BeCl_2$ (c) PCl_3 (d) $MgCl_2$

(e) $AlCl_3$ (f) CCl_4 (g) $SiCl_4$

Solution: (a) $H_3BO_3 + HCl$ (b) $Be(OH)_2 + HCl$ (c) $H_3PO_3 + HCl$ (d) $Mg(OH)_2 + HCl$

(e) $Al(OH)_3 + HCl$ (f) No hydrolysis (g) $Si(OH)_4 + HCl$

Illustration 6: **Which is correct order of hydrolysis**

(a) $NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$ (b) $CCl_4 < SiCl_4 < GeCl_4 < SnCl_4 < PbCl_4$

(c) $LiCl < BeCl_2 < BCl_3$ (d) Both (a) and (c)

Solution: **Ans. (d)**

covalent character $\propto$ rate of hydrolysis

Illustration 7: **Why CCl_4 do not undergo hydrolysis.**

Solution: Due to absence of vacant orbital in central atom.

Illustration 8: **Why SF_6 do not undergo hydrolysis.**

Solution: Due to steric crowding on central atom by the presence of 6 flourine atoms.

Illustration 9: **Why NF_3 do not undergo hydrolysis.**

Solution: N & F both belong to 2^{nd} period have lone pair to donate but both do not have vacant orbital to accomodate lone pair.

BEGINNER'S BOX-3

1. The product formed in the reaction,

$BCl_3 + H_2O \longrightarrow$ Product is –

(1) $H_3BO_3 + HCl$ (2) $B_2O_3 + HOCl$ (3) $B_2H_6 + HCl$ (4) No reaction

2. $AlCl_3$ on hydrolysis gives –

(1) $Al_2O_3.H_2O$ (2) $Al(OH)_3$ (3) Al_2O_3 (4) $AlCl_3.6H_2O$

3. Which one of the following compounds gives methane on treatment with water ?

(1) Al_4C_3 (2) CaC_2 (3) Mg_2C_3 (4) SiC

4. The number of types of bonds between two carbon atoms in calcium carbide is :-

(1) One sigma, two pi (2) One sigma, one pi

(3) Two sigma, one pi (4) Two sigma, two pi

5. Which of the following gives propyne on hydrolysis

(1) Al_4C_3 (2) Mg_2C_3 (3) B_4C (4) La_4C_3

6. Which of the following does not act as lewis acid ?

(1) BF_3 (2) $SnCl_4$ (3) CCl_4 (4) SF_4

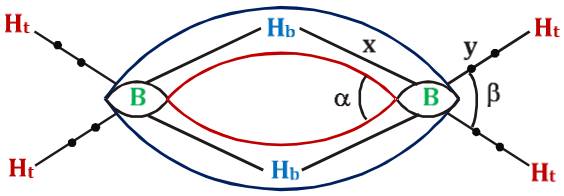
Dimerisation / polymerisation

Types of Dimerisation

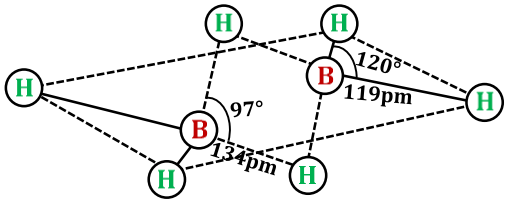
by 3 centre -2e⁻ bond	by 3 centre -4e⁻ bond
eg. B_2H_6	eg. $(BeCl_2)_2$
$(BeH_2)_2$	$(BeCl_2)_n$
$(BeH_2)_n$	$(AlCl_3)_2$
$Al_2(CH_3)_6$	$(ICl_3)_2$
$Ga_2(CH_3)_6$	

(A) By banana Bond or by 3 Centre–2e⁻ bond or by e⁻ deficient bond

(a) B_2H_6



α < β = BA
x > y = BL
H_b—Bridge H
H_t—Terminal H



2 Centre–2e⁻ bonds = 4 3 Centre–2e⁻ bonds = 2 structure of diborane, B_2H_6

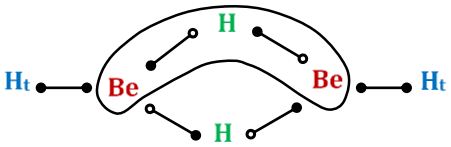
Hybridisation state of boron is sp^3

It is electron deficient molecule and act as a lewis acid.

- All four terminal hydrogen and two boron atoms are present in same plane both bridging H are present in perpendicular plane.
- If substitution reaction takes place then maximum four terminal hydrogen atoms can be substituted.

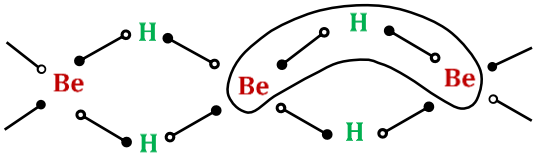
$B_2H_6 + 4CH_3–Cl \rightarrow B_2H_2(CH_3)_4 + 4HCl$

(b) $(BeH_2)_2$ (dimer of BeH_2 in vapour state)



- Hybridisation state of Be is sp^2
- Planar
- electron deficient molecule

(c) $(BeH_2)_n$ (polymer of BeH_2 in solid state)



- Hybridisation state of Be is sp^3
- Non-planar
- electron deficient molecule

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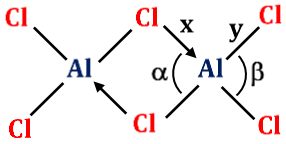
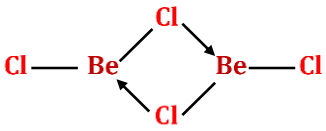
(B) By-coordinate Bond / 3 Centre–4e⁻ bond

(a) Al_2Cl_6 (dimer of $AlCl_3$ in liquid or solid state)



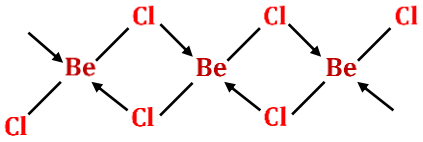
- $\alpha < \beta$; Order of bond angle
- x > y ; Order of bond length
- Hybridisation state of Al is sp^3
- Non-planar
- octet of Al is complete so it is not e^- deficient

(b) $(BeCl_2)_2$ (dimer of $BeCl_2$ in vapour state)



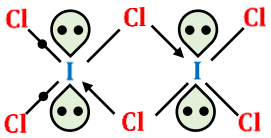
- Hybridisation state of Be is sp^2
- Planar
- electron deficient molecule

(c) $(BeCl_2)_n$ (polymer of $BeCl_2$ in solid state)



- Hybridisation state of Be is sp^3
- Non-planar
- octet of Be is complete so it is not e^- deficient

(d) I_2Cl_6 (dimer of ICl_3)



- Hybridisation state of I is sp^3d^2
- Planar
- e^- rich molecule (12 e^-)

Note :

(i) BCl_3, BBr_3 & BI_3 do not form dimer due to smaller size of boron & large size of halogen (due to more steric repulsion)

(ii) BF_3 cannot form dimer due to presence of back bonding.

(iii) AlF_3 cannot form dimer due to its ionic nature.

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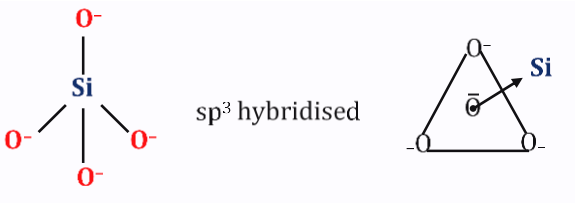
BEGINNER'S BOX-4

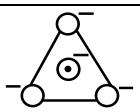
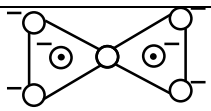
1. Which of the following statements is incorrect in relation to the structure of diborane
   (1) All the terminal B-H bond length are equal
   (2) The terminal B–H bond is a 2-centre 3-electron bond
   (3) The terminal B–H bond is a 2-centre 2-electron bond
   (4) The bridge is a 3-centre 2-electron bond
2. Which of the following statements is correct in the context of diborane (B_2H_6) ?
   (1) There are 12 valence electrons-three from each of the two boron atoms and six from the six hydrogen atoms
   (2) Two of the six hydrogen atoms form two bridges between two boron atoms
   (3) The two bridging hydrogen atoms are in a plane perpendicular to the rest of the molecule and prevent rotation between the two boron atoms
   (4) All of these
3. Which of the following does not exist in free form ?
   (1) BF_3 (2) BCl_3 (3) BBr_3 (4) BH_3

Compounds of silicon

(A) Silicates

- Naturally occurring minerals.
- Si and O atoms have poor tendency to form π bond, so these silicates anion have tendency to form polymer.
- Basic structural unit is SiO_4^{-4}.



Silicate	No. of shared oxygen per unit	General formula	Structure	Example
Ortho silicate	0	SiO_4^{-4}		Zircon ($ZrSiO_4$)
Pyro silicate	1	$Si_2O_7^{-6}$		Hemi morphite $Zn_3Si_2O_7.Zn(OH)_2.2H_2O$)

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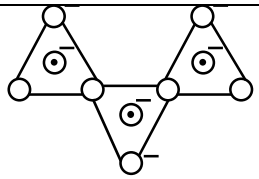
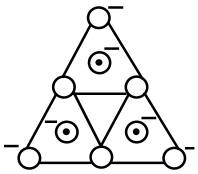
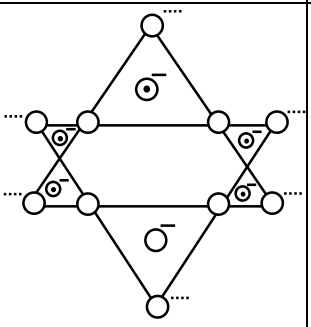
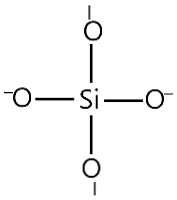
Single chain silicate	For terminal unit-1 For centre unit-2	$(SiO_3^{-2})_n$ But not true formula of single chain silicate		$Ca_2Cu_2Si_3O_{10}$ (Kinoite)
Cyclic silicate	2	$(SiO_3^{-2})_n$ True formula of cyclic silicate		Beryl ($Be_3Al_2Si_6O_{18}$)
Sheet silicate	3	$(Si_2O_5^{-2})_n$		Talc $(Mg_3(OH)_2)(Si_2O_5)_2$
3-D silicate	4	$(SiO_2)_n$		Silica (SiO_2)

Some important example of silicates

(1) Sodium Zeolite $[Na_2Al_2Si_2O_8]/[Na_2O.Al_2O_3 . 2SiO_2.xH_2O]$

(i) It is a 3-D silicate

(ii) It is used as :

(a) an ion exchanger for softening of hard water.

(b) a catalyst in petrochemical industries for cracking of hydrocarbon & isomerisation.

Ex. ZSM-5 (Zeolite) is used to convert ethyl alcohol into petrol.

(2) Silicon dioxide (SiO_2)/Silica

- Occurs in different forms like quartz, cristobalite and tridymite.
- Almost non-reactive due to strong Si–O bond.
- However, it is attacked by NaOH and HF
- Quartz is used to develop accurate clocks, modern radio & TV broadcasting & mobile radio communication.

TG: @Chalnaayaaar

- Silica gel is used as a drying agent.
- Kieselguhr is amorphous form of silica which is used in filtration plants.

(a) $2NaOH + SiO_2 \longrightarrow \underset{\text{water glass}}{Na_2SiO_3} + H_2O$

(b) $SiO_2 + 4HF \longrightarrow 2H_2O + SiF_4$

$SiF_4 + 2HF \longrightarrow \underset{\substack{\text{hexa fluro}\\ \text{silicic acid}}}{H_2[SiF_6]}$

- This process is also known as **Etching of glass**.

(B) silicones

Silicones are organosilicone polymer which contain R_2SiO as a repeating unit.

Properties :

(i) Silicones are chemically inert due to the presence of strong sigma bond.

(ii) Silicones have water repelling nature due to presence of alkyl group.

(iii) Silicones are electric insulator due to absence of free electrons.

Preparation :

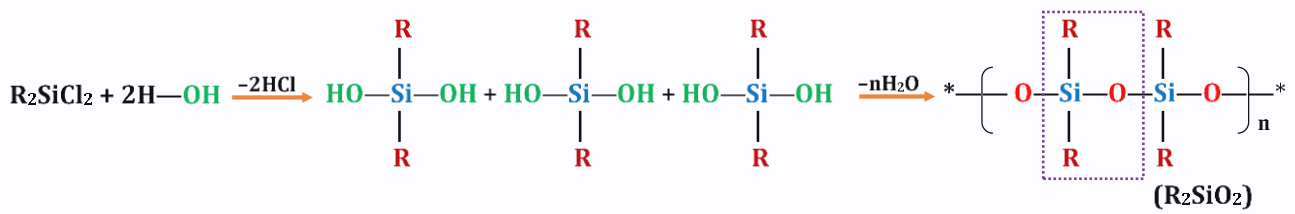
Alkyl chloro silane $\xrightarrow{\text{hydrolysis}}$ product $\xrightarrow{\text{condensation}}$ silicones

R_3SiCl : used to stop chain length of silicones

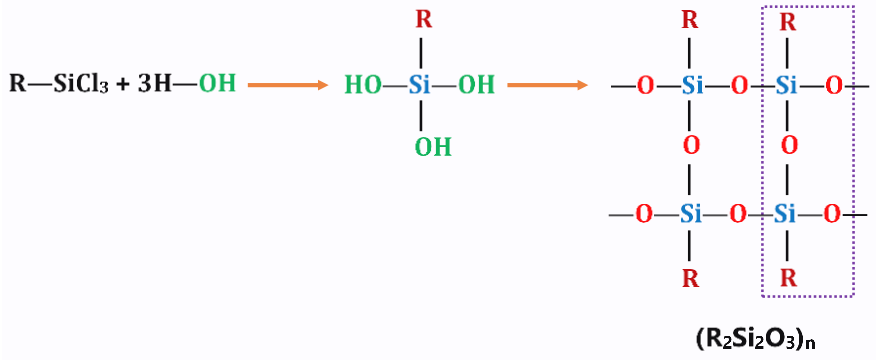
R_2SiCl_2 : used to form single chain silicones

$RSiCl_3$: used to form cross link silicones

(a) Linear chain silicone (single chain silicones)



(b) Cross linked silicone/Double chain silicone



BEGINNER'S BOX-5

1. Silicones have the general formula

(1) SiO_4^{4-} (2) $Si_2O_7^{6-}$ (3) $(R_2SiO)_n$ (4) $(SiO_3)_n^{2-}$

2. Consider the following route of reactions

R_2SiCl_2 + Water $\rightarrow$ (A) $\xrightarrow{\text{Polymerisation}}$ (B)

Compound(B) in above reaction is

(1) Dimer silicone (2) Linear silicone

(3) Cross linked silicone (4) Polymerisation of (A) does not occur

Allotropes

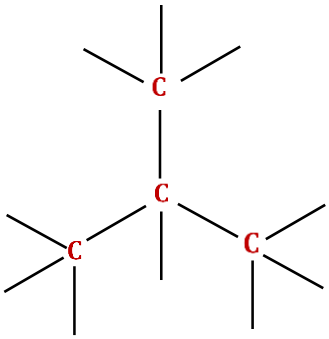
(A)

Allotropes of Carbon

Crystalline	Amorphous
Ex. Diamond	Ex. Coke
Graphite	Charcoal
Fullerene	Coal, C-lamp black

Special Point :

DIAMOND



Each carbon atom is bonded with four other carbon atoms

sp^3 hybridisation

tetrahedral structure

Insulator due to the absence of free electrons

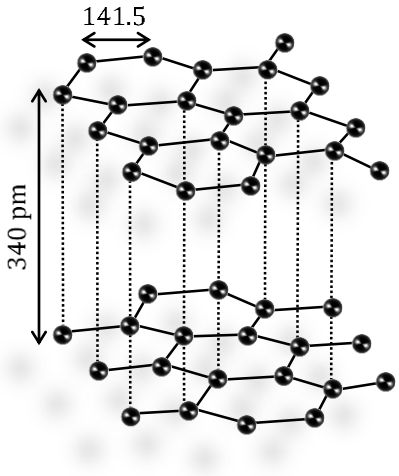
Hard due to the presence of strong sigma bond and 3D structure

Density = 3.35 gm/cm^3

High melting point (giant molecule)

Bond length (C—C) = 1.54 Å

GRAPHITE



Each carbon atom is bonded with three other carbon atoms

sp^2 hybridisation

Hexagonal layer structure

Conductor due to the presence of delocalised electrons

Soft due to the presence of weak van der Waals forces between two layers

Density = 2.22 gm/cm^3

Low melting point

Bond length (C—C) = 1.41Å

TG: @Chalnaayaaar

(i) Thermodynamically graphite is more stable than diamond.

(ii) Aqueous solution of graphite is known as **aquadag**.

(iii) Graphite is also known as **plumbago (used in lead pencil)**

(iv) Graphite is used as a dry lubricants.

(v) **Hardest allotrope** of carbon is diamond, **softest allotrope** is lamp black, **purest allotrope** is fullerene

Fullerene

- C-60 & C-70 are common forms of fullerene.
- C-60 is also known as Buckmeinster fullerene (Bucky ball)
- There are 32 rings $32 \begin{cases} 12 \text{ pentagonal} \\ 20 \text{ hexagonal} \end{cases}$
- Each carbon atom bonded with 3 other carbon by sigma & double bond (resonance).
- sp^2 hybridisation & aromatic in nature.

Dangling Bond

In diamond or graphite some surface carbon atoms have free valency. These carbon atoms form new bonds with impurities. These new bonds are known as dangling bond.

BEGINNER'S BOX-6

1. The false statement about the diamond will be
(1) The C-C bond length is larger than C=C, and C≡C
(2) It is a molecular solid
(3) Dangling bond present along the surface and therefore have some impurities like hydrogen
(4) Diamond is bad conductor

2. Which one of the following is incorrect statement for graphite ?
(1) It has layer structure and each carbon atom sp^2 hybridised
(2) It has a football like structure.
(3) Most stable allotropes of carbon
(4) None

3. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite.
(1) Is an allotropic form of diamond
(2) Has molecules of variable molecular masses like polymers
(3) Has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bounds.
(4) Is a non-crystalline substance

Boron family, introduction and properties

Introduction

The p-block elements are those elements of the periodic table in which the differentiating electron (or the last electron) enters the p-subshell of the last (outermost) shell. Since the maximum capacity of any atomic orbital is of two electrons with opposite spins (Pauli's principle), the maximum number of electrons that can be accommodated in any p-subshell is six. As a result, the p-block of the periodic table consists of six groups 13 (III A), 14(IV A), 15(V A), 16(VI A), 17(VIIA) and 18 (zero group). On the basis of electronic configuration, the element **He** is to be excluded from the p-block as its last electron enters the s-subshell of the last shell.

Boron family

Boron is a typical non-metal, Aluminium is a metal but shows many chemical similarities to Boron, and Gallium, Indium and Thallium are almost exclusively metallic in character.

General characteristics

(A) Physical properties :

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), can exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to Thallium.

(B) Oxidation state

(a) These elements show +1 and +3 oxidation states.

(b) B & Al shows only +3 oxidation state. While other elements show +1 and +3 oxidation state.

(c) +1 oxidation state is more stable on moving down the group due to increase in inert pair effect.

(d) Relative stability of M^+ and M^{3+} ions may be given as :

$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

$B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$

Tl^+ ion is more stable than Tl^{3+} ion and thus, $T\ell^{3+}$ ion changes to $T\ell^+$ ion therefore acting as an oxidising agent.

$T\ell^{3+}$ compounds + $2e^- \longrightarrow T\ell^+$ compounds

(C) Chemical properties

(a) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3\,O_2\,(g) \xrightarrow{\Delta} 2\,E_2O_3\,(s);\ 2E(s) + N_2\,(g) \xrightarrow{\Delta} 2\,EN\,(s).$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of Indium and Thallium are basic in their properties.

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BEGINNER'S BOX-7

1. Boron form covalent compound due to
(1) Higher ionization energy (2) Lower ionization energy
(3) Small size (4) Both (1) and (3)

2. Which of the following has highest non-metallic characteristic ?
(1) Gallium (2) Indium (3) Boron (4) Aluminium

3. Which one of the following is a correct statement ?
(1) The hydroxide of aluminium is more acidic than that of boron
(2) The hydroxide of boron is basic while that of aluminium is amphoteric
(3) The hydroxide of boron is acidic while that of aluminium is amphoteric
(4) The hydroxides of both boron and aluminium are amphoteric

4. Boron reacts with air to give –
(1) B_2O_3 (2) BN (3) Both (4) None

Chemistry of boron- Orthoboric acid, Borax

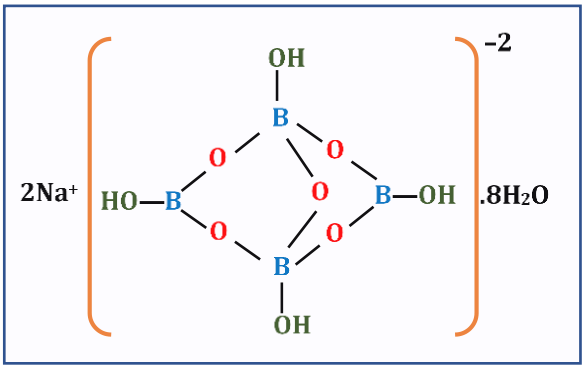
(A) Structure of Boron: Elemental boron exists in B_{12} form.

(B) Chemical properties : It exists in five allotropes, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. However, it is attacked at high temperature by strong oxidising agents such as a mixture of hot and concentrated H_2SO_4 and HNO_3 or Na_2O_2. But amorphous form is brown and chemically active.

(C) Compounds of Boron

(I) Borax ($Na_2B_4O_7.10H_2O$)

$2Na^+ [B_4O_5 (OH)_4]^{-2}.8H_2O$



Important points :

B–O–B linkage = 5

Total B–O bonds = 14

Two B-sp^2 hybridised

Two B-sp^3 hybridised

Properties :

(i) Borax is a white powder, less soluble in cold water due to stable H-bonds within the molecule of borax, but more soluble in hot water, due to breaking of H-bonds present in borax, so that new H-bonds can easily form with water molecule.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(iii) Action of heat.

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it converts into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

Borax-bead test :

Borax reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

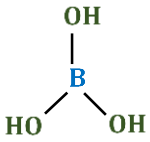
$$Na_2B_4O_7{\cdot}10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}} ; CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

Ni^{2+} - Brown, Cu^{2+} - Pale blue, Co^{2+} - Dark blue, Mn^{2+} - Pink, Cr^{3+} - Green.

Uses : It is used

1. in borax bead test
2. in purifying gold
3. as flux during welding of metals
4. in the production of glass.

(II) Ortho boric acid [H_3BO_3/$B(OH)_3$]



$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$$

Properties:

It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:

$$B(OH)_3\ (aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+\ (aq). \qquad pK_a = 9.25.$$

It therefore, functions as a Lewis acid and not as a proton donor like most acids.

Heating effect :

When heated it first forms metaboric acid (HBO_2) and then boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100°C} HBO_2 \xrightarrow{160°C} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Orthoboric acid is greasy to touch, less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together into two dimensional sheets with almost hexagonal symmetry. The layers are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.

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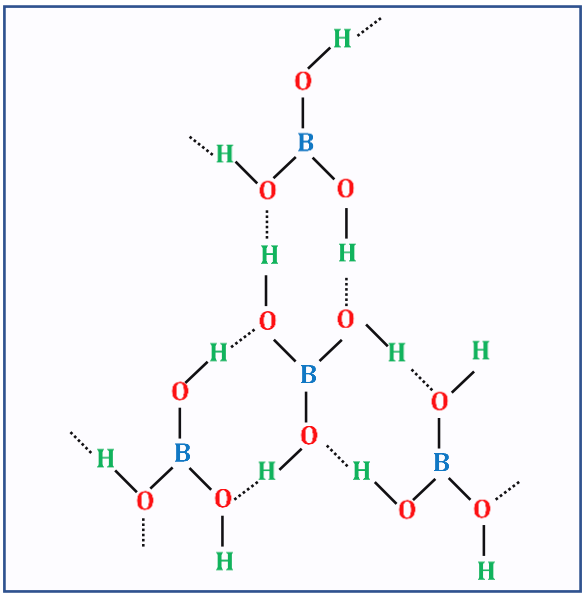

Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Uses :

1. It is an antiseptic and its water solution is used as an eyewash.

2. It is also used in glass, enamel and pottery industry.

(III) Diborane (B_2H_6)

Binary compounds of B with H are called boron hydrides or boranes.

Preparation :

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiF + 3AlF_3$

(ii) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$

(iii) $2BF_3 + 6NaH \xrightarrow{453K} B_2H_6 + 6NaF$ **(Industrial method)**

Properties :

(i) B_2H_6 is colourless gas and highly reactive (boiling point 183 K).

(ii) It catches fire spontaneously in air and explodes with O_2. Reaction with oxygen is extremely exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta H = -2160 \text{ kJ mol}^{-1}$$

Mixture of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

At red-hot, the boranes decomposes to give boron and hydrogen.

(iii) Reaction with water is instantaneous.

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

(iv) The electron deficient 3c-2e B–H–B bridges are sites of nucleophilic attack.

Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [BH_4]^-$$

Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

$$2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \leftarrow N(CH_3)_3$$

The reaction with ammonia depends on conditions.

$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3}$ $B_2H_6 \cdot 2NH_3$ or $[H_2B(NH_3)_2]^+ [BH_4]^-$ (ionic compound).

$\xrightarrow[\text{higher temperature}(>200°C)]{\text{Excess } NH_3}$ $(BN)_x$ **boron nitride/Inorganic graphite/Borazone**

$\xrightarrow[\text{higher temperature}(>200°C)]{\text{Ratio } 2NH_3:1B_2H_6}$ $B_3N_3H_6$ **borazine/Inorganic benzene/Borazole**

Borazine is much more reactive than benzene. Borazine readily undergoes addition reactions which do not occur with benzene. Borazine also decomposes slowly and may be hydrolysed to NH_3 and boric acid at elevated temperature. If heated with water, $B_3N_3H_6$ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$

Illustrations

Illustration 10: **The geometry of $[B(OH)_4]^-$ ion is**

(1) Triangular (2) Hexagonal
(3) Rectangular (4) Tetrahedral

Solution: **Ans. (4)**

In $[B(OH)_4]^-$ boron is sp^3 hybridised and it is tetrahedral.

Illustration 11: **Orthoboric acid**

(1) Donate proton to form $H_2BO_3^-$
(2) Accept proton of form $H_4BO_3^+$
(3) Donate OH^- to form $H_2BO_2^+$
(4) Accept OH^- to form $[B(OH)_4]^-$

Solution: **Ans. (4)**

H_3BO_3 acts as a lewis acid and accepts an OH^- ions to form $[B(OH)_4]^-$

Illustration 12: **Boric acid heated to red hot gives**

(1) HBO_2 (2) H_2BO_2 (3) B_2O_3 (4) Borax

Solution: **Ans. (3)**

Illustration 13: **Boric acid is used in carom boards for smooth gliding of pawns because :-**

(1) H_3BO_3 molecules are loosely chemically bonded and hence soft
(2) Its low density makes it fluffy
(3) It is chemically inert with the plywood
(4) H-bonding in H_3BO_3 gives it a layered structure

Solution: **Ans. (4)**

Illustration 14: **Diborane readily reacts with water forming –**

(1) Diborate and O_2 (2) Boric acid and O_2
(3) Boric acid and H_2 (4) Diborate and H_2

Solution: **Ans. (3)**

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

TG: @Chalnaayaaar

Chemistry of aluminium

Compounds of Aluminium

(a) Aluminium chloride – $AlCl_3$:

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous $AlCl_3$ is a deliquescent white solid.

Preparation :

(i) By dissolving aluminium, Al_2O_3, or $Al(OH)_3$ in dilute HCl :

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$ $\quad Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

The solution obtained is filtered and crystallized when the crystals of $AlCl_3.6H_2O$ are obtained.

(ii) By heating a mixture of Al_2O_3 and coke and passing chlorine over it.

$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3$ (anhydrous) $+ 3CO\uparrow$

(b) Alum :

(i) Introduction :

(a) Alums are double salt of sulphates with their general formula $M_2SO_4.M'_2(SO_4)_3.24H_2O$ where M= monovalent radical like Na^+ , K^+, NH_4^+ and M' = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

(b) The different alums are -

(i) Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(ii) Chrome alum $K_2SO_4\ Cr_2(SO_4)_3.\ 24\ H_2O$

(iii) Iron alum $(NH_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$

(iv) Ammonium alum $(NH_4)_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

(c) In alums each metal ion is surrounded by six water molecules.

(d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

(e) It is salt of (SA + SB) and (SA + WB) thats why aqueous solution of alum is acidic.

(ii) Properties :

(a) It is a white crystalline solid highly soluble in water.

(b) On heating it undergoes dehydration and swells up.

(c) It is highly acidic in aqueous solution due to the hydrolysis of aluminium sulphate to sulphuric acid

(d) It is a double salt and its aqueous solution gives reaction of all the constituents ions K^+, Al^{+3}, SO_4^{-2}.

(iii) Uses :

(i) Alum is used to stop bleeding. (ii) It is used for purification of water.

BEGINNER'S BOX-8

1. Which of the following statements about H_3BO_3 is not correct

(1) It is a strong tribasic acid

(2) It is prepared by acidifying an aqueous solution of borax

(3) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds

(4) It does not act as proton donor but acts as a Lewis acid by accepting hydroxyl ion

2. The hardest substance amongst the following is

(1) Be_2C (2) Graphite (3) B_4C (4) SiC

3. Which of the following is known as inorganic benzene

(1) Borazine (2) Boron nitride (3) *p*-dichlorobenzene (4) Borazone

TG: @Chalnaayaaar

Introduction and Allotropes of Carbon family

- Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points.

General characteristics

Physical properties

- All group 14 elements are solid.
- They have higher melting point and boiling point than 13 group elements.

Chemical properties

Reaction with O_2

- All elements when heated with O_2 form two types of oxide (MO and MO_2).
- SiO only exist at high temperature.

Reactivity towards H_2O

- C, Si and Ge do not react with H_2O.
- Sn decomposes steam to form dioxide and H_2 gas.

$$Sn + 2H_2O\ (steam) \longrightarrow SnO_2 + 2H_2$$

- Pb is unaffected by H_2O due to formation of protective layer of oxide.

Catenation property

- C has maximum tendency of catenation due to formation of strong C–C bond.
- On moving down the group tendency of catenation decreases due to increase in size.
- Lead does not show catenation.

Compounds of carbon (Oxides of carbon family)

(A) Carbon Monoxide (CO)

(I) Preparation

(i) It is formed together with CO_2, when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red- hot carbon; this reaction is of importance in metal extractions.

$$C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)}$$

(ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid.

$$HCOOH\ (liq) \xrightarrow[conc.H_2SO_4]{373K} CO_{(g)} + H_2O$$

(iii) If oxalic acid is dehydrated in the same way, CO_2 is formed as well.

$$H_2C_2O_4 \xrightarrow[-H_2O]{conc.H_2SO_4,\Delta} CO + CO_2$$

(iv) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as **water gas** or **synthesis gas**.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{473—1273K} CO_{(g)} + H_{2(g)}\ (water\ gas).$$

When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas**.

$$2C_{(s)} + O_{2\,(g)} + 4N_{2(g)} \xrightarrow{1273K} 2CO_{(g)} + 4N_{2(g)}\ (Producer\ gas).$$

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

(II) Physical Properties

(i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2. It is sparingly soluble in water and is a neutral oxide. CO is toxic, because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the

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haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes oxygen deficiency, leading to unconsciousness and then death.

(B) Carbon Dioxide (CO_2)

Preparation :

(i) Complete combustion of carbon containing compounds.

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

(ii) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips.

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(\ell)$$

(iii) Industrially it is produced as a by-product during the manufacturing of quicklime and in fermentation processes.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g); \qquad C_6H_{12}O_6(aq)\{glucose\} \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Properties :

(i) It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacturing of soda water and fizzy drinks.

(ii) CO_2 is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimes at –78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

(iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows : $H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

H_2CO_3 / HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO_2 is evolved.

(iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(liq) \; ; \; CaCO_3(s) + H_2O(liq) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

The above reaction accounts for the formation of temporarily hard water.

(v) Carbon dioxide, which is normally present to the extent of ~ 0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as :

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

By this process plants make food for themselves as well as for animals and human beings. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

(vi) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non–supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

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Carbides and Hydrides of Carbon family

(C) Carbides :

Carbides are of three types according to the type of bonding

(i) Salt like carbides (Ionic carbides)

(ii) Covalent carbides (Giant molecular carbides)

(iii) Interstitial carbides (Metallic carbides).

(I) Salt like carbides (Ionic carbides) :

(a) These are formed by strong electropositive elements of groups 1, 2 and 13

(b) These are transparent crystalline substances and do not conduct electric current in the solid state.

(c) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons.

(i) **Methanides** (**Methides**) – Methanides are the carbides which give methane on hydrolysis.

They contain C^{4-} ions.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(ii) **Acetylides** – These are the carbides which yield acetylene on hydrolysis.

They contain the ion C_2^{2-} $(C\equiv C)^{-2}$

e.g. : CaC_2

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \text{ or } C_2^{2-} + 2H^+ \longrightarrow C_2H_2$$

Most of these carbides have ionic NaCl - type of structure.

(iii) **Allylides** – These carbides give methylacetylene or allylene ($CH_3–C\equiv CH$) on hydrolysis.

They contain C_3^{4-} ions. The only example of this class is Mg_2C_3

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3–C\equiv CH$$

(II) Covalent carbides (Giant molecular carbides)

(a) Covalent carbides are the compounds of carbon with elements having similar electronegativity.

(b) These are covalent, polymeric, thermally stable, extremely hard, high melting and technically inert solid.

(c) B_4C and SiC are two main covalent carbides.

(III) Interstitial / Metallic carbides

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retains their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremely hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

Illustrations

Illustration 15: Which of the following is methanide –

(1) Be_2C (2) Al_4C_3 (3) Mg_2C_3 (4) Both (1) and (2)

Solution: **Ans.(4)**

Both Be_2C and Al_4C_3 has C^{4-} ion and on hydrolysis gives CH_4.

Illustration 16: Consider the following chemical reaction –

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

(1) CO is an oxidising agent (2) CO is reducing agent

(3) CO is neutral towards litmus (4) CO acts as catalyst

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Solution: **Ans. (2)**

CO is reducing agent because it readily accepts oxygen to from CO_2. CO is used as reducing agent to reduce many metallic oxides into metals in metallurgy.

Illustration 17: **Consider the following chemical reaction**

$$\text{HCOOH(aq.)} \xrightarrow{X,\Delta} \text{CO(g)} + \text{H}_2\text{O(g)}$$

Formic acid

In the above reaction (X) is –

(1) Conc. H_2SO_4 (2) Conc. HCl (3) Conc. HNO_3 (4) Dil. HNO_3

Solution: **Ans. (1)**

Illustration 18: **Living in the atmosphere of CO is dangerous because it –**

(1) Reduces organic matter of tissues

(2) Dries up the blood

(3) Combines with haemoglobin of blood and makes it incapable to absorb oxygen

(4) Combines with O_2 present inside to form CO_2

Solution: **Ans. (3)**

Illustration 19: **The ionic carbide is**

(1) ZnC (2) TiC (3) SiC (4) CaC_2

Solution: **Ans. (4)**

BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4		
	Ans.	**1**	**4**	**4**	**4**		
BEGINNER'S BOX-2	**Que.**	1	2	3	4		
	Ans.	**1**	**4**	**1**	**1**		
BEGINNER'S BOX-3	**Que.**	1	2	3	4	5	6
	Ans.	**1**	**2**	**1**	**1**	**2**	**3**
BEGINNER'S BOX-4	**Que.**	1	2	3			
	Ans.	**2**	**4**	**4**			
BEGINNER'S BOX-5	**Que.**	1	2				
	Ans.	**3**	**2**				
BEGINNER'S BOX-6	**Que.**	1	2	3			
	Ans.	**2**	**2**	**3**			
BEGINNER'S BOX-7	**Que.**	1	2	3	4		
	Ans.	**4**	**3**	**3**	**3**		
BEGINNER'S BOX-8	**Que.**	1	2	3			
	Ans.	**1**	**3**	**1**			